Supporting Information

Ga-doped Cu/H-nanozeolite-Y catalyst for selective hydrogenation/hydrdeoxygenation of lignin-derived chemicals

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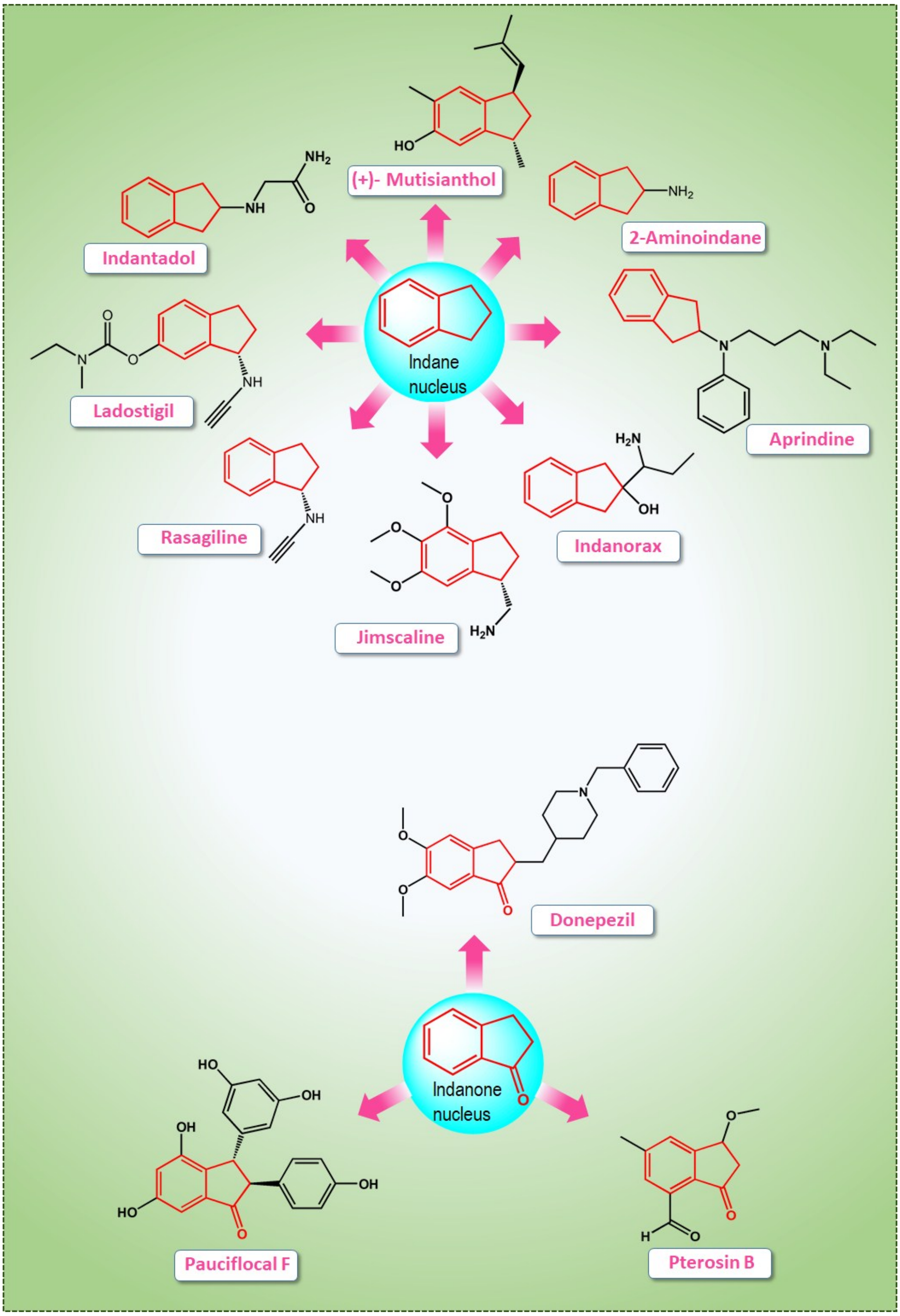

Fig. S1 Example of some commercial drugs derived from indane and indanone.[1]

Table S1. Summary of the reported HDO reactions of vanillin, acetovanillone, and cinnamaldehyde over various types of heterogeneous catalysts.

Catalysts	Feed	Catalyst	Solvent	P_{H2} (MPa)	T (°C)	t (h)	Conv. (%)	Selectivity (%)	Reference
Noble metal-based catalyst	Vanillin	Au/CNTs	H_2O^a	1.0	200	6	100	75 (Creosol)	[2]Yang *et al*. RSC Adv. 2014, 4, 31932.
	Vanillin	Ru/CNTs	H_2O^a	1.0	150	3	100	96 (Creosol)	[3]Yang *et al*. Catal. Comm. 2014, 47, 28.
	Vanillin	Pd/CM180[b]	H_2O^a	1.0	100	1	>99	94 (Creosol)	[4]Zhu *et al*. Green Chem. 2014, 16, 2636.
	Vanillin	Pd/SO_3H-MIL-101(Cr)	H_2O	1.0	90	1	100	98.4 (Creosol)	[5]Zhang *et al*. J. Mater. Chem. A. 2015, 3, 17008.
	Vanillin	Pd/$CN_{0.132}$	H_2O	1.0	150	6	100	100 (Creosol)	[6]Xu *et al.* J. Am. Chem. Soc. 2012, 134, 16987.
	Vanillin	Pd/SWNT[c]-SiO_2	H_2O^a	0.34	100	6	100	45 (Creosol)	[7]Crossley *et al.* Science 2010, 327, 68.
	Vanillin	Pd/TiO_2@N-C	H_2O	1.0	150	6	95.5	>99.5 (Creosol)	[8]Wang *et al.* ChemSusChem 2014, 7, 1537.
	Vanillin	Pd/C	AcOH	1.0	55	24	>99	99 (Creosol)	[9]Wang *et al*. Tetrahedron, 2006, 62, 6107.
	Vanillin	Pd/POP[d]	IPA	1.0	140	18	96.5	98.2 (Creosol)	[10]Singuru *et al*. ChemCatChem 2017, 9, 2550.
	Vanillin	Pd/PRGO[e]/Ce-MOF	H_2O	1.0	100	5	100	>99 (Creosol)	[11]Ibrahim *et al*. ChemCatChem. 2017, 9, 469.
	Cinnamaldehyde	Pt/CoAl-MMO[f]	EtOH	2.0	80	2	99.7	72.5 (Cinnamyl alcohol)	[12]Tian *et al.* J. Catal. 2015, 331, 193.
	Cinnamaldehyde	Pd/HHT[g]	Dioxane	--	80	5	100	60.0 (Hydrocinnamaldehyde)	[13]Rao *et al.* Nature Comm., 2017, 8, 340.
Non-noble-metal based-catalyst	Vanillin	$CoMoS_x/Al_2O_3$	Dodecane	5.0	300	6	53	23 (Creosol)	[14]Jongerius *et al.* J. Catal.,2012, 285, 315.
	Vanillin	Ni/N-doped CB[h]	H_2O	0.5	150	2	74.4	64.6 (Creosol)	[15]Nie *et al*. Green Chem. 2017, 18, 2900.
	Vanillin	Cu@PMO[i]	MeOH	4.0	180	18	100	90 (Creosol)	[16]Petitjean *et al*. Green Chem. 2016, 18, 150.
	Acetovanillone	Cu@PMO	MeOH	40.0	180	18	100	>95[d] (4-ethylguiuacol)	
	Vanillin	Ga-doped Cu/HNZY	MeOH	1.0	160	2	100	>99 (Creosol)	This work
	Acetovanillone		MeOH	1.0	160	5	100	>99 (4-ethylguiuacol)	
	Cinnamaldehyde		MeOH	1.0	160	2	98	58 (Hydrocinnamaldehyde)	

[a]mixed with equal amount of decalin.

[b]CM180 = carbonaceous microspheres-180 (hydrothermal temp.); [c]SWNT= single-walled Nanotube; [d]POP = porous organic polymer; [e]PRGO = partially reduced graphene oxide; [f]MMO = mixed metal Oxide; [g]HHT = high heat-treated (for stacked cup carbon nanotubes); [h]CB = carbon black; [i]PMO = porous metal oxide.

The conversion (%) and selectivity (%) was calculated using the following formulae:

$$Conversion\ (\%) = \frac{mol\ of\ the\ reactant\ left}{initial\ mol\ of\ the\ reactant} \times 100,$$

$$Selectivity\ (\%) = \frac{mol\ of\ the\ product\ produced}{mol\ of\ the\ reactant\ consumed} \times 100.$$

Quantification of the selected products (mol%) from cinnamaldehyde was done using an Agilent Technologies 6890N equipped with an Rxi-5Sil MS as the column and a flame ionization detector (FID). External standards were prepared for 3,3-dimethoxypropyl benzene (DMPB), 2, 3-dihydroindenol (DHO), 1-allyl-4-methoxybenzene (AMB), and propenylbenzene (PNB) using MeOH as a solvent. The concentrations of the other peaks were quantified using the effective carbon number method (ECN), as proposed by Schofield.[17] The formula to quantify the rest of the compounds is given as

$$C_i = \frac{C_{ref}}{A_{ref}} * A_i * \frac{n_{eff,ref}}{n_{eff,i}}, \qquad (1)$$

where C is the concentration, A is the area shown by the chromatogram in GC/FID, and n_{eff} is the effective carbon number. Index *i* and *ref* denote the selected compound with unknown concentration and reference, respectively. Depending on the structure of the compounds, toluene and hydrocinnamyl alcohol were used as references.

Calculation of metal dispersion, metal surface area and metal particle size of bimetallic Ga-Cu/HNZY catalyst using N_2O pulse chemisorption

V = Total N_2 volume (ml)
S = Stoichiometry factor (2)
W = Sample weight (mg)
C = Metal content (wt%)
C1 = Content of metal 1
C2 = Content of metal 2
A_w = Atomic weight of metal
A_w1 = Atomic weight of metal 1
A_w2 = Atomic weight of metal 2
A = area occupied by a surface metal (nm^2)
A1 = area occupied by a surface metal 1 (nm^2)
A2 = area occupied by a surface metal 2 (nm^2)
ρ = Metal density ($g.cm^{-3}$) of metal
ρ1 = Metal density ($g.cm^{-3}$) of metal 1
ρ2 = Metal density ($g.cm^{-3}$) of metal 2
$N_0 = 6.023 \times 10^{23}$
Volume of 1 mole N_2 gas at STP = 22414 ml

For monometallic

$$\text{Metal dispersion (D\%)} = \left(\frac{V * S * 1000}{22414 * W}\right) * 100 * \left(\frac{A_w}{C/100}\right)$$

For bimetallic A_w/C = M1 + M2

$$\text{Metal dispersion (D\%)} = \left(\frac{V * S * 1000}{22414 * W}\right) * 100 * \left(M1 + M2\right) * 100$$

$$M1 = \left(\frac{C1}{C1 + C2}\right)\left(\frac{A_w1}{C1 + C2}\right) \qquad M2 = \left(\frac{C2}{C1 + C2}\right)\left(\frac{A_w2}{C1 + C2}\right)$$

For monometallic

$$\text{Metal surface area (SA}_m\text{)} = \left(\frac{A * B}{22414 * W/1000}\right) * 6.023 \times 10^{23} * \left(\frac{A * 10^{-18}}{C/100}\right)$$

For bimetallic,

Here,

$$A/C = \left(X1 + X2\right) \qquad X1 = \left(\frac{C1}{C1 + C2}\right)\left(\frac{A1}{C1 + C2}\right) \quad X2 = \left(\frac{C2}{C1 + C2}\right)\left(\frac{A2}{C1 + C2}\right)$$

For monometallic

$$\text{Metal particle size (d}_p\text{)} = \left(\frac{6000}{SA_m * \rho}\right)$$

For bimetallic,

Here,

$$\rho = \left(Y1 + Y2\right) \qquad Y1 = \left(\frac{C1}{C1 + C2}\right)\rho 1 \quad Y2 = \left(\frac{C2}{C1 + C2}\right)\rho 2$$

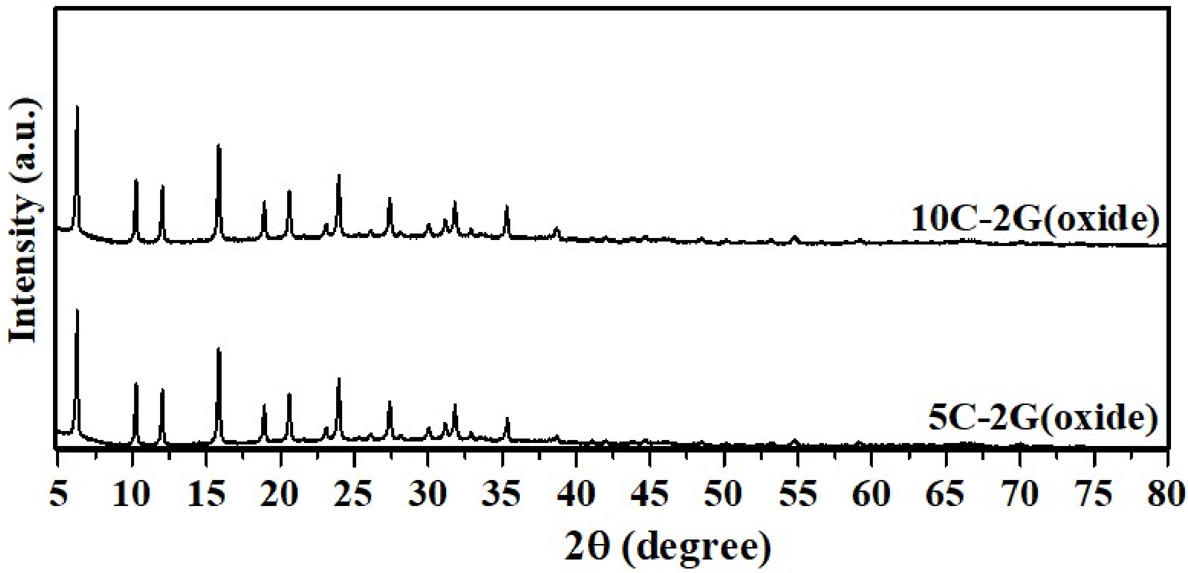

Fig. S2 XRD patterns of the Ga-doped Cu/HNZY (oxide form).

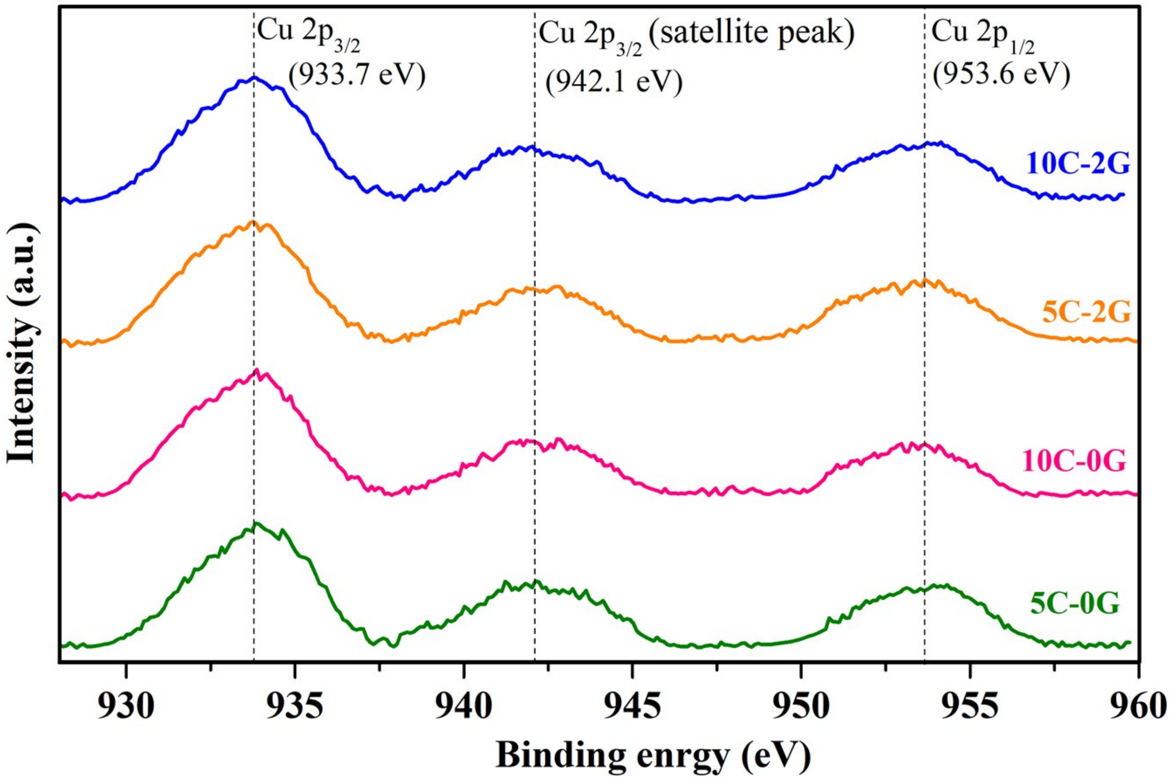

Fig. S3 XPS core-level spectra of the Cu 2p state of Cu-based catalysts (oxide form).

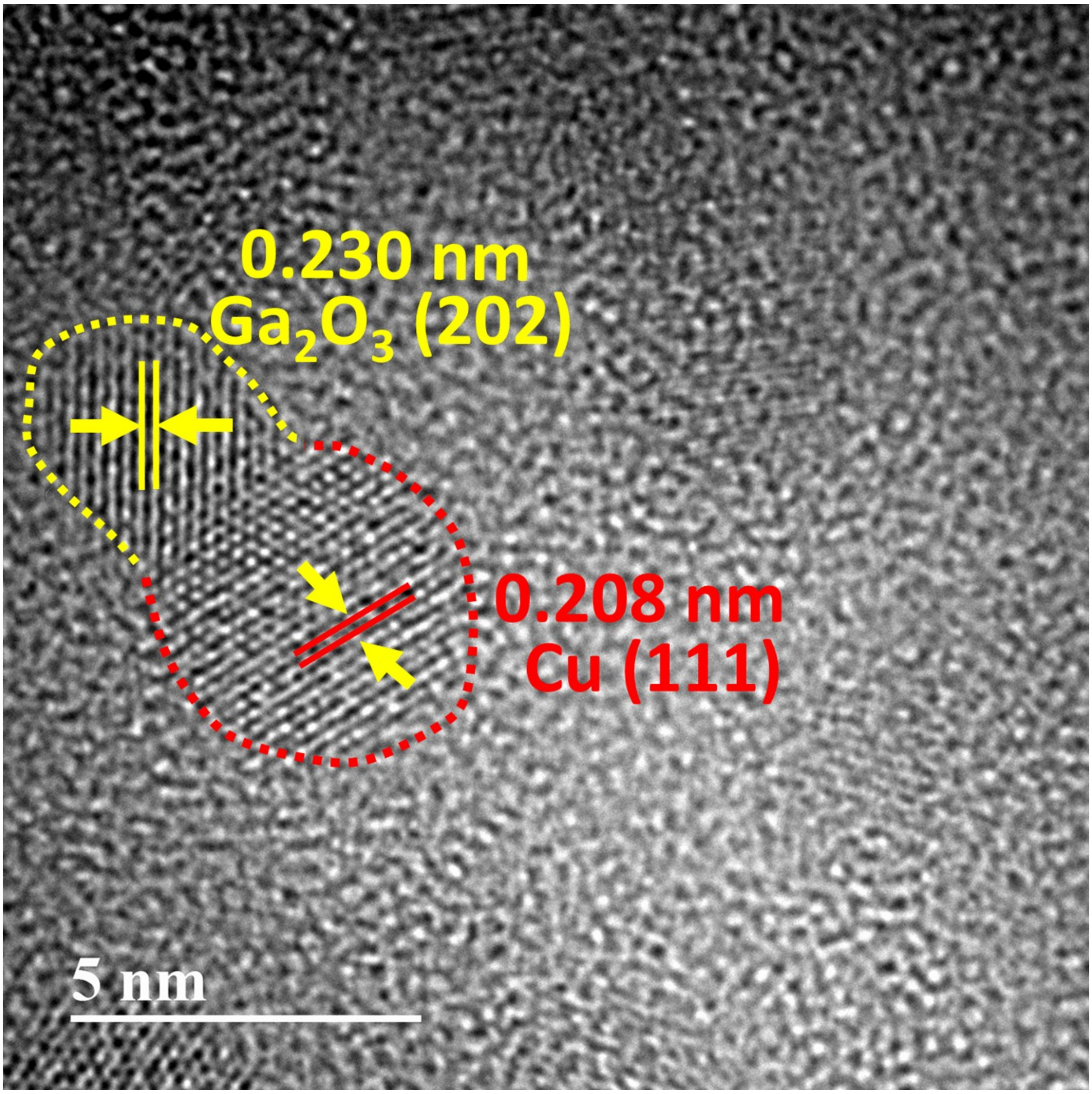

Fig. S4 High-magnification HR-TEM image of the 5C-2G catalyst. Yellow and red lines indicate the (202) and (111) lattice plane corresponding to Ga_2O_3 and Cu, respectively.

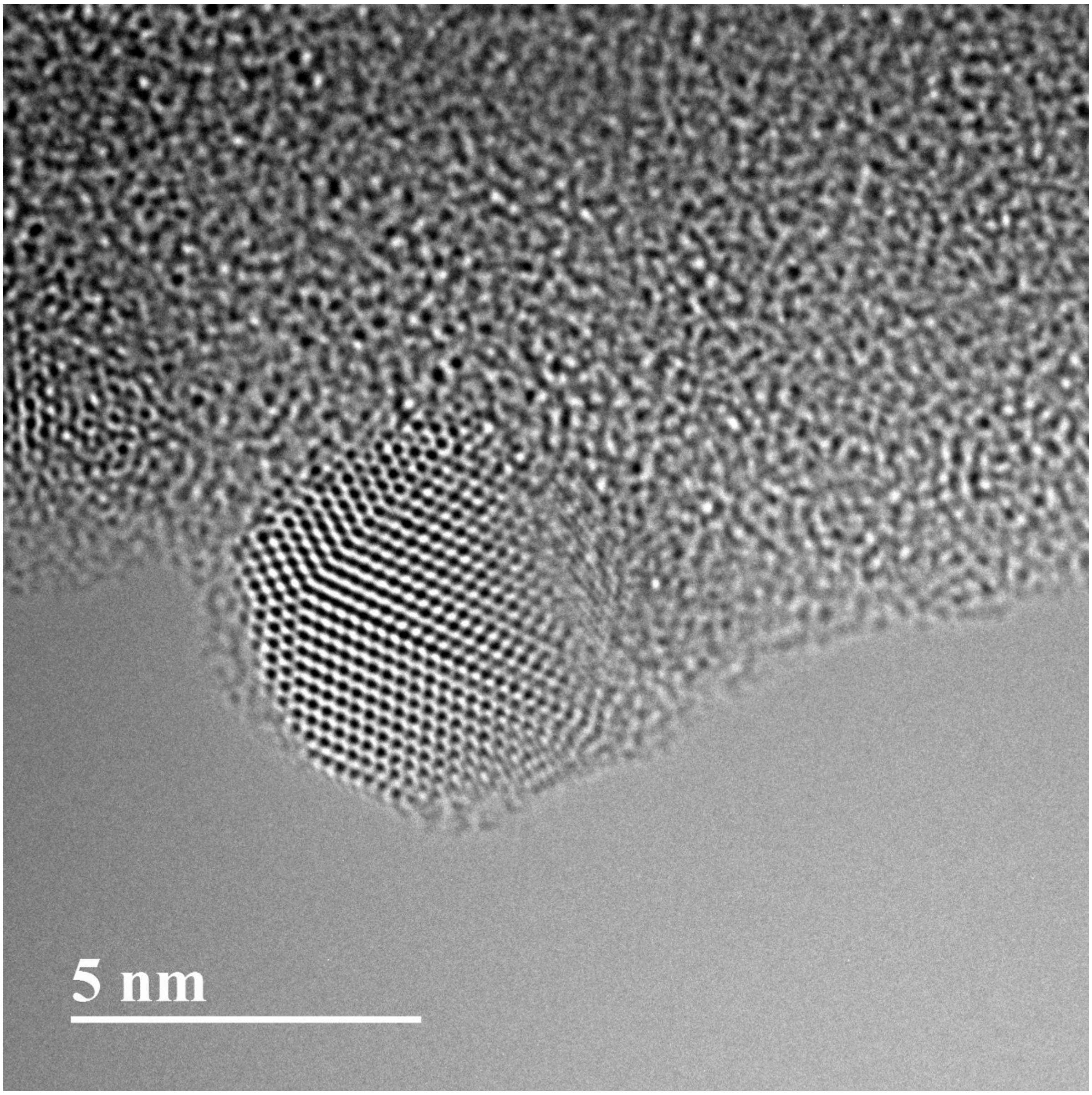

Fig. S5 High-magnification HRTEM image of the 10C–2G catalyst.

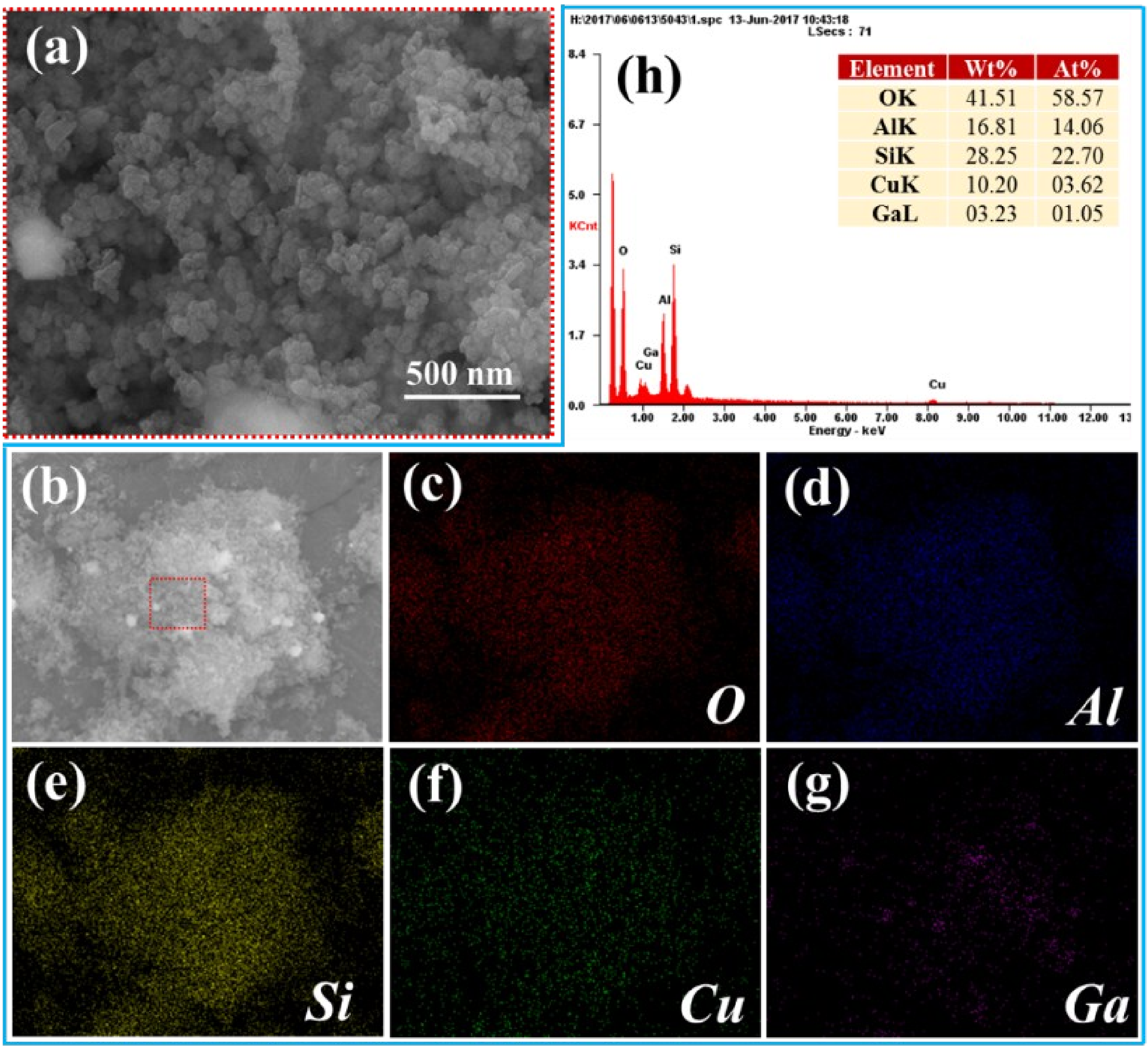

Fig. S6 (a) FE-SEM image, (b) –(g) elemental mapping of O, Al, Si, Cu, and Ga, respectively, and (h) corresponding EDS graph of the 10C–2G catalyst.

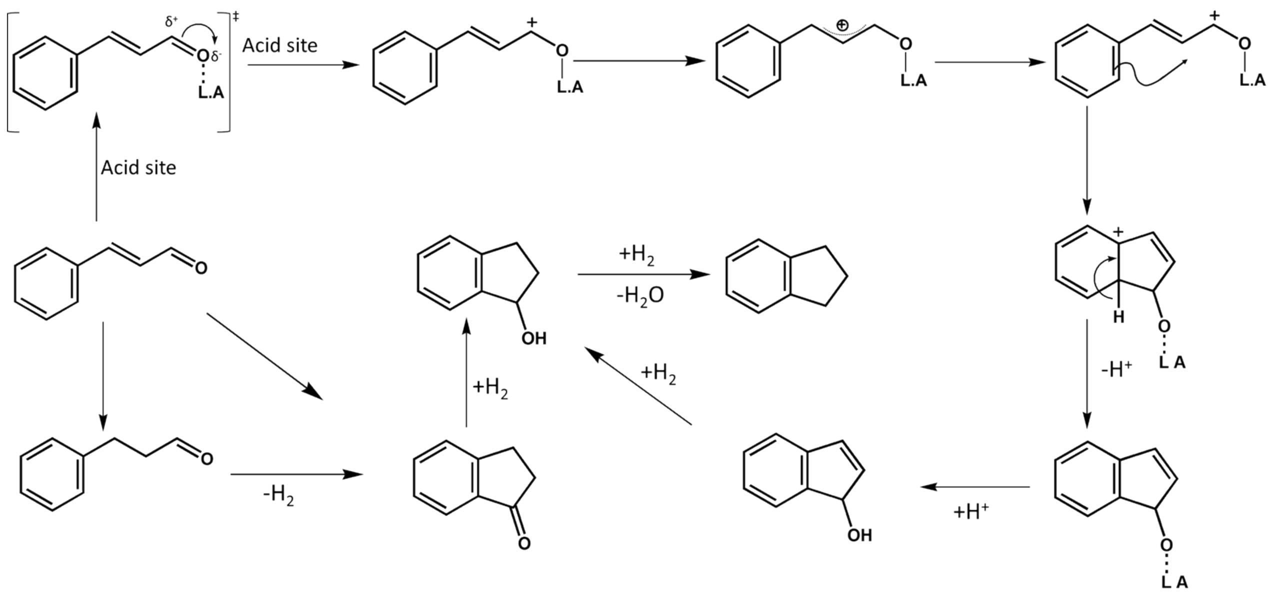

Fig. S7 Plausible reaction mechanism of cinnamaldehyde cyclization/hydrodeoxygenation to indane derivatives.

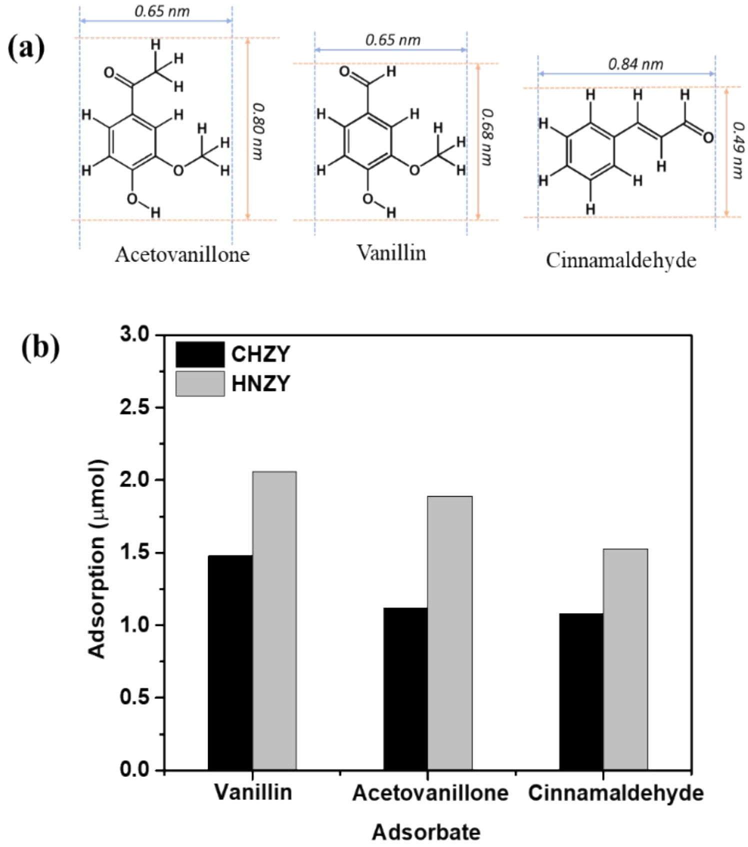

Fig. S8 (a) Molecular size of the adsorbates calculated by the ACD/3D software and (b) adsorption study of the adsorbates with 20 mg of adsorbent (CHZY and HNZY) at room temperature. The adsorption test showed that the adsorption capacity of the adsorbates was higher in the HNZY support as compared to the C-HZY support. (Note: pore channel size of typical zeolite-Y = 0.74 x 0.74 x 0.74 nm)

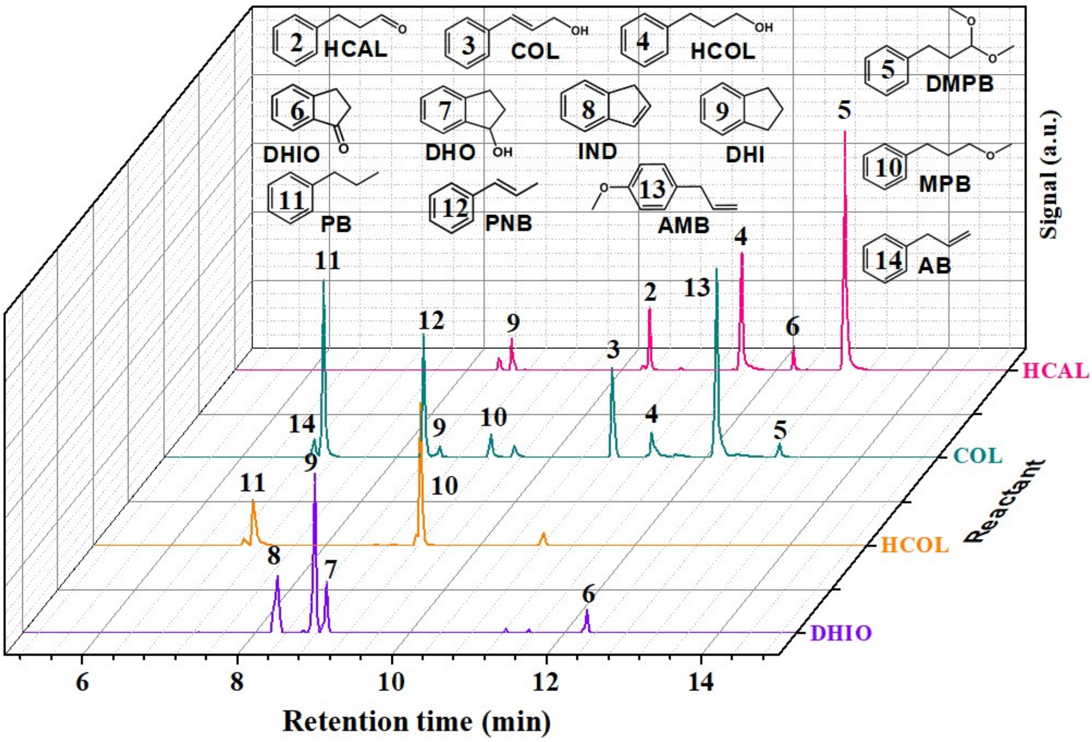

Fig. S9 GC-TOF/MS chromatograms of the liquid products obtained from the selective hydrogenation/hydrodeoxygenation of hydrocinnamaldehyde (HCAL, 2), cinnamyl alcohol (COL, 3), hydrocinnamyl alcohol (HCOL, 4) and 2,3-dihydroindanone (DHIO, 6) over the 10C–2G catalyst. Reaction conditions: 1 g feed, 35 ml MeOH, 0.25g catalyst, 1 h, 180 ^{o}C, and an initial H_2 pressure of 1 MPa.

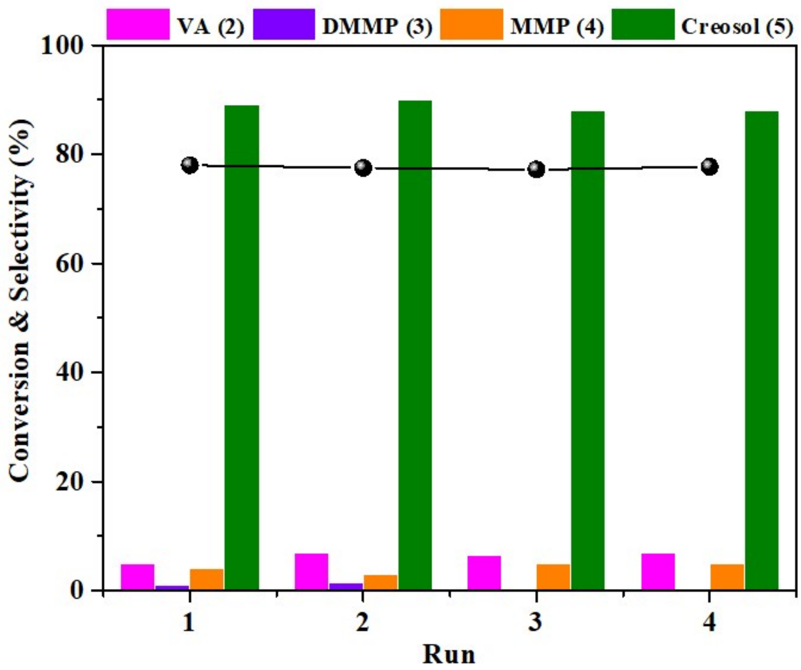

Fig. S10 Recyclability test of the 10C-2G catalyst with high feed-to-catalyst ratio of 13.3:1 Reaction condition: 1 g vanillin, 0.075 g catalyst, 35 mL methanol, 160 ^{o}C, initial H_2 pressure of 1 MPa, and 2 h.

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